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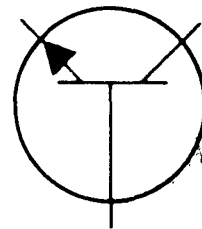
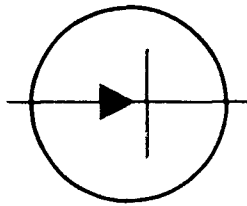


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WESTINGHOUSE ELECTRIC CORPORATION

32 North Main Street

Dayton 2, Ohio

**Interim Technical Documentary
Progress Report No. 4**

**GALLIUM ARSENIDE DENDRITE
SINGLE CRYSTAL PROGRAM**

Contract No. AF 33(657)-8162

**Period Covered
25 November 1962 to 24 February 1963**

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I. INTRODUCTION

All three furnaces were operating during this report period; the 7" furnace continuously, the 14" furnace during the latter half of the period, and the 24" furnace became operational at the end of the period. When the 14" furnace was brought into operation, the 7" furnace was modified to include a method of stirring the melt to help in the more rapid attainment of stoichiometry. Several experiments indicate the success of the stirring method but the method of controlling arsenic pressure is still poor and the furnace is being modified to have a side-arm control zone similar to that in the 14" and 24" furnaces.

Primitive dendrites and some rudimentary ribbons have been pulled in the 14" and 24" furnaces. Some multi-dendrite sheet 3-4" long and 1/2" wide, has been pulled in the 7" furnace. This sheet material is free of inclusions and is of device quality.

ABSTRACT

The 7", 14", and 24" dendrite furnaces were operated during this period. Magnetic stirring and an improved arsenic pressure control system were used.

Successful achievement of multi-dendrite sheet growth is ascribed to use of a narrow spaced three-twin seed. Some of the material pulled was used to make solar cells.

The solar cell process has been revised so that alloying of contacts and diffusion are accomplished in one operation. Reproducibility has thereby been improved.

II. DENDRITE PREPARATION

A. Experimental Problems and Progress

1. Crystal Growth - 7" Exploratory Furnace

Crystal growth techniques have evolved from the state described in the Third Quarterly Report to a point where multi-dendrite sheet can be grown. Figures 1 and 2 show opposite sides of two multi-dendrite sheets, the larger being 3-4" long and greater than 1/2" wide over part of its length. The length of the sheet, in this case, was limited solely by the furnace geometry. This material was free of inclusions and has been used for the fabrication of solar cells, as described later.

In addition to general improvement in thermal geometry and stoichiometry control, the successful achievement of multi-dendrite sheet growth can be ascribed to using a very narrow spacing three-twin seed. Until seeds having this narrow spacing (2.5 μ and 1.5 μ thick lamella) were used, "wing" formation presented a severe problem to continuous growth. The wings which grew at 60° to the downwards growth direction usually grew out in such a way that they were caught under the lid and thus prevented continuous growth. The use of the narrow twin seed has essentially eliminated this difficulty. Branches at 60° which do develop were found to result from the loss of a twin thus giving rise to a two twin structure at the edge of the growth button. This structure in turn permits wing growth.

Unexpected results, however, have become apparent during the growth of material using narrow twin spacing seed. In germanium, silicon, or indium antimonide, a narrow twin spacing

prevents multi-dendrite web from forming; this does not appear to be the case in gallium arsenide, as shown in Figures 1 and 2.

As the structure is pulled, additional dendrites initiate and cause widening. This type of growth morphology is not the ordinary branching due to wing formation since these lateral additions are not crystallographically limited. As pulling continues, some of the dendrites occasionally stop growing, thus narrowing the structure. The result of the widening then is the irregular structure shown in Figures 1 and 2. The cause of the multi-dendrite growth is unknown. It is possible that gallium arsenide propagates in a different fashion at the tip in comparison with, say pure indium antimonide, or it may be that the dendritic growth of GaAs is particularly sensitive to traces of impurities or slight non-stoichiometry. Albon and Owen⁽¹⁾ observed impurity effects on the case of growth of indium antimonide in the "321" direction for certain twin spacings. Heavy doping of germanium also gives rise to propagation in the $\langle 110 \rangle$ direction even when narrow twin spacings are used. It is not clear, therefore, whether a slight excess gallium or arsenic is affecting growth at the tip or whether even narrower twin spacings are required in the gallium arsenide seed to prevent multi-dendrite growth.

Material pulled now is usually free from inclusions of any kind; this indicates that the melt is not far removed from stoichiometry during pulling. Long times (2-3 hours) are still required, however, to introduce the correct amounts of arsenic, at least in the furnace design used for the exploratory 7" furnace.

(1) Albon, N. and Owen, A. E., submitted to J. Appl. Phys.

In order to see whether very careful stoichiometry control will help eliminate multi-dendrite growth, two techniques are being developed. These are a) stirring of the melt, and b) improved control of the arsenic pressure. The latter approach has already been followed in the 14" puller and some of the results obtained will be discussed later.

Stirring of the melt should improve pulling conditions from two points of view. First, the long periods of time required to homogenize the melt will be eliminated; this, in turn, will reduce the time spent by a gallium-rich melt in contact with the crucible. Since, under certain conditions, gallium is a strong reducing agent, this procedure should reduce the total impurity content introduced into a melt during a run. Secondly, stirring should eliminate the existence of any pockets of non-homogeneous melt which might exist. Non-homogeneity of the melt is particularly important during dendrite growth since growth would stop if such a region intercepted the dendrite tip. It should be pointed out that these problems do not arise during Czochralski growth since there is ample stirring due to rotation of the Czochralski crystal.

Stirring has been achieved with 7" furnace by using alternating crossed magnetic fields in the melt. These fields were generated by passing large currents (300 amps) at 60 cycles through two pancake coils and also the furnace work coil. The coils were arranged so that the resulting field gave a tumbling motion to the melt. The affects due to stirring are presently being evaluated. The method of arsenic control in the 7" furnace is being converted to that used in the 14" puller. It is hoped that these two modifications will greatly improve control over the composition of the melt.

2. Crystal Growth - 14" Furnace

During this report period, the construction of the 14" puller was completed and runs were begun. Temperature profiles determined inside and outside the arsenic control zone sidearm showed a direction relationship. Therefore, it is possible to determine the control temperature within a few degrees by measuring the outside temperature.

A schematic diagram of this furnace is given in Figure 3. All of the important components of this furnace are indicated on the diagram.

Several runs were made in this furnace before mechanical difficulties with the pull rod and pulling mechanism were eliminated. In these experiments, seedings were attempted at several control temperatures and growth buttons and very short dendrites were obtained. The lowest control temperature used was 610°C and it was found that no long wait for equilibrium was necessary as had been the case with the 7" furnace. This thermocouple temperature indicates a temperature inside the sidearm 622°C. All of the buttons and/or short dendrites resulting in these experiments were potted and lapped and, under microscopic examination, no gallium inclusions were detected.

After several minor changes took care of the mechanical problems previously mentioned, more extensive experiments in pulling were carried out. These experiments indicated definite problems with temperature gradient in the system. The surface was definitely too cold. The seedings which took place branched very quickly on the surface and prevented any length from being pulled. Some adjustments have been made in the location

of the R.F. coil in an attempt to increase the surface temperature; and some improvement has been noted, but not enough to overcome the difficulty. Due to the nature of the gallium arsenide and the consequent involved furnace construction necessary, changes of this sort take much time and results are necessarily slow in coming out. In addition to changing the coil position, changes in the length of the quartz shield and the height of the second lid above the melt are also being investigated.

In all experiments with this furnace, there has been no need for long periods of waiting for equilibrium conditions to be established. This lack of need to wait is demonstrated by the lack of inclusions of gallium even when the seedings had taken place within 1/2 hour after the gallium arsenide was molten. Using the deep crucible, there has been no occurrence of the bubbling phenomenon observed in the 7" furnace with a shallow crucible. The surfaces of the small dendrites have been very smooth and differences between opposite faces have been generally less than previously found. These observations give some encouragement that the rather straight-forward modifications in furnace design (particularly the sidearm As-control technique) will be valuable not only in cutting the time required to reach stoichiometry but also in improving the quality and uniformity of GaAs sheet.

3. Crystal Growth - 24" Furnace

The 24" pulling furnace has been completed and placed in operation. Several dummy runs were made with neither arsenic nor gallium arsenide in the system in order to establish the temperature profiles in the furnace. When it had been

established that the temperature profiles were acceptable, the furnace was run using arsenic but no gallium arsenide. The purpose of these experiments was to check out the arsenic control zone and the leakage of the pistons under operating conditions. The results of these experiments proved satisfactory and actual runs were begun.

The initial run in the furnace with gallium arsenide had to be terminated before any pulling experiments could be started due to the failure of the thermocouple measuring and controlling the melt temperature. On a second run, some primitive "claw" dendrites were grown from a polycrystalline seed. Some experience in the operation of the furnace and the seeding and growth of gallium arsenide dendrites in this furnace were the most important result of this experiment.

The main problem in the use of this furnace up to this time has been the burn out of the control thermocouple. The attempted solution was to lengthen the thermocouple protection tube to extend below the water cooled bottom flange to provide a more positive arsenic trap. This solution has apparently been successful.

III. SOLAR CELL PREPARATION

Some revisions in the solar cell preparation process were made during the past quarter. The concentration of the HNO_3 in the prediffusion etch was cut in half. In the diffusion process, the zinc is still kept at a higher temperature than the GaAs, but the arrangement in the furnace has been improved. The wafers are now brought up to temperature before diffusion, and the zinc is placed in a second zone. The position of the zinc boat is controlled from one end of the furnace tube, the GaAs boat from the other end.

A grid pattern is sandblasted onto the polished face of the GaAs wafer to be processed. A silver alloy is evaporated onto the grid pattern, and lead, followed by nickel, is evaporated onto the opposite surface of the wafer. Wafers, zinc, and arsenic are inserted into the furnace tube; the wafers and zinc are held at the cool ends of the tube while flushing with inert gas takes place. The wafers are then pushed into a 600°C flat temperature zone and allowed to come up to temperature. At the end of this preheating period, the wafers have been brought to a uniform temperature and the contacts have been alloyed to the GaAs surfaces. Diffusion is then initiated by pushing the zinc boat into the 700°C location in the left-hand zone (Figure 4). Diffusion is terminated by pulling the GaAs boat from the hot zone to the cool end of the tube. The cells are then solder dipped and their edges are lapped.

Reproducibility with this process is quite good up to the point of solder dipping. Cells have been made in this way starting with dendritic material, which gave results comparable to Czochralski and boat-grown material. Cell efficiencies as high as 5.7% have been obtained.

IV. RESULTS AND CONCLUSIONS

The 7", 14" and 24" pulling furnaces were operated and some usable material was obtained from the 7" furnace. When the difficulties have been worked out of the larger furnaces, sheet with more widely spaced dendrites should be realizable. A novel solar cell fabrication process has been developed in which contacts are applied prior to diffusion. This process has shown improved reliability with respect to reproducibility of cell performance.

V. PROGRAM FOR FUTURE WORK

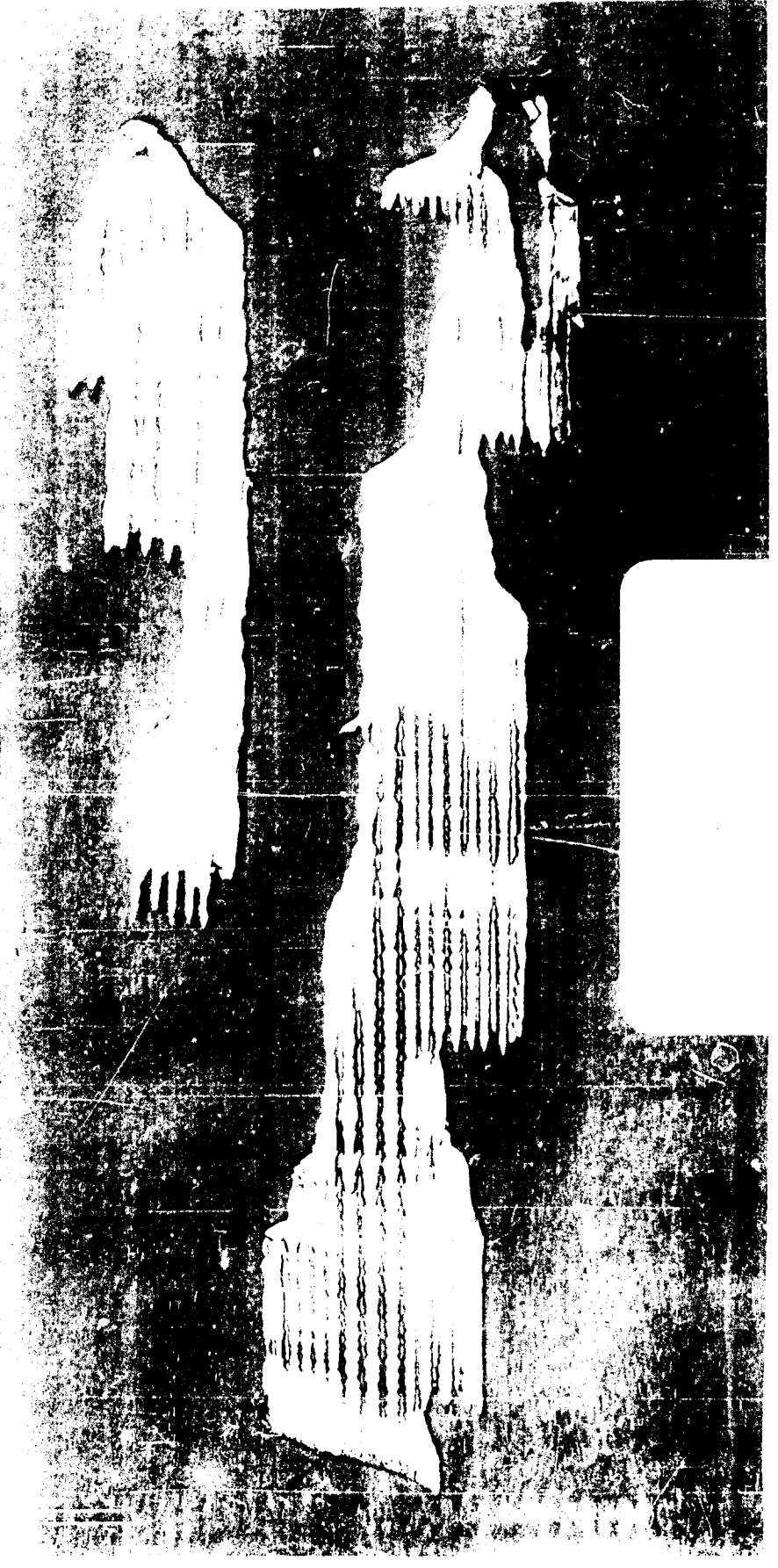
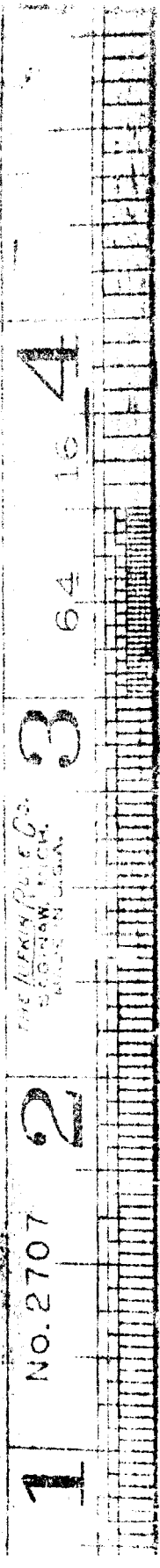
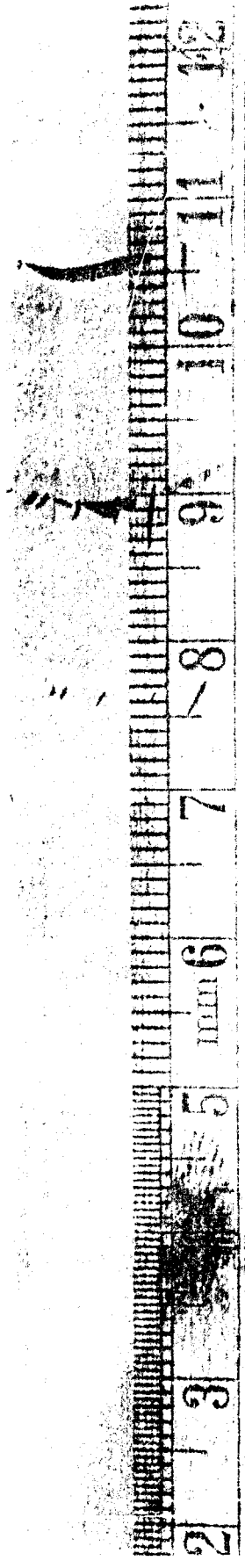
A. Dendrite Preparation

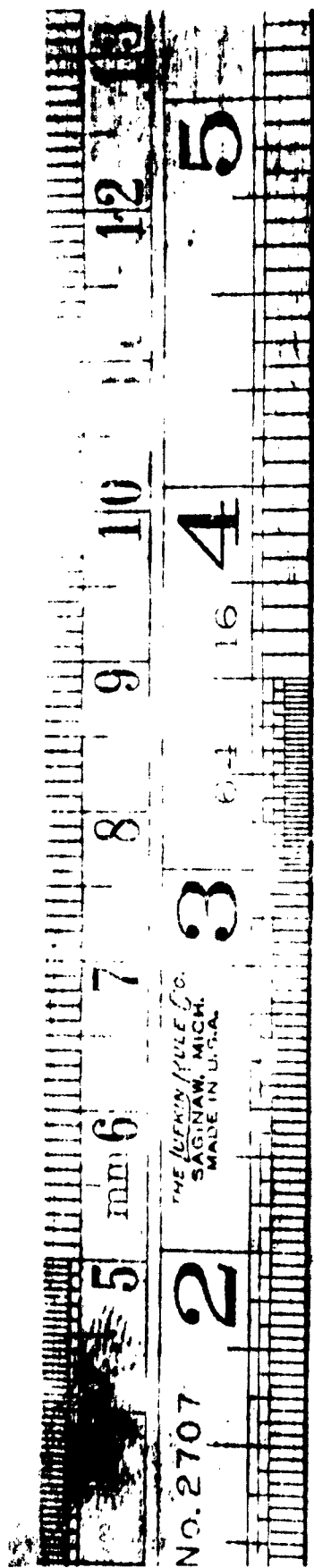
All three furnaces will be in operation and various experiments are planned for each. The 7" furnace with stirring and the new control zone will be used to determine the source of and to eliminate the bubbling phenomenon noticed in the shallow crucible. The 14" furnace and 24" furnace will be operated to obtain dendritic and web material and experiments of various coil locations and crucible and lid configurations will be carried out to adjust the thermal gradients. The major portion of the total effort will be placed on GaAs webbed dendrites during the following months.

B. Solar Cell Preparation

Although considerable progress has been made in preventing degradation of cell voltage by solder dipping, further work remains to be done. The cell currents; although fairly consistent from run to run, are still too low. It may be necessary to decrease the junction depth or decrease surface reflectivity in order to increase the current. The grid lines on our present pattern were made wide (.020) to simplify the task of learning how to put on the grids. When we have learned how to put on a solder-dipped grid without deteriorating cell voltage, finer grid lines will be used.

Since the zinc diffusion process now seems to be fairly well refined, the possibility of effecting an improvement in junction characteristics will be investigated.





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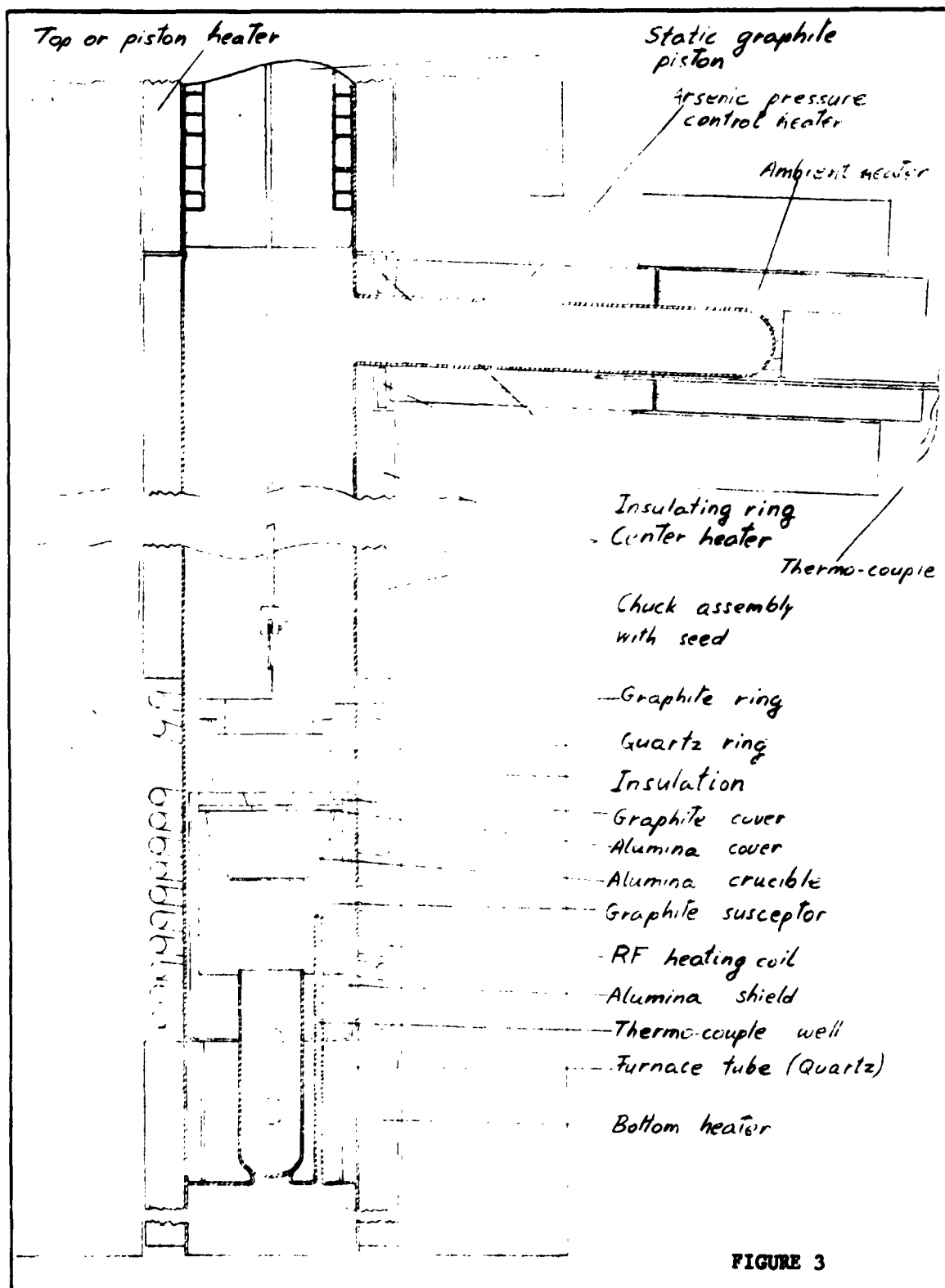


FIGURE 3

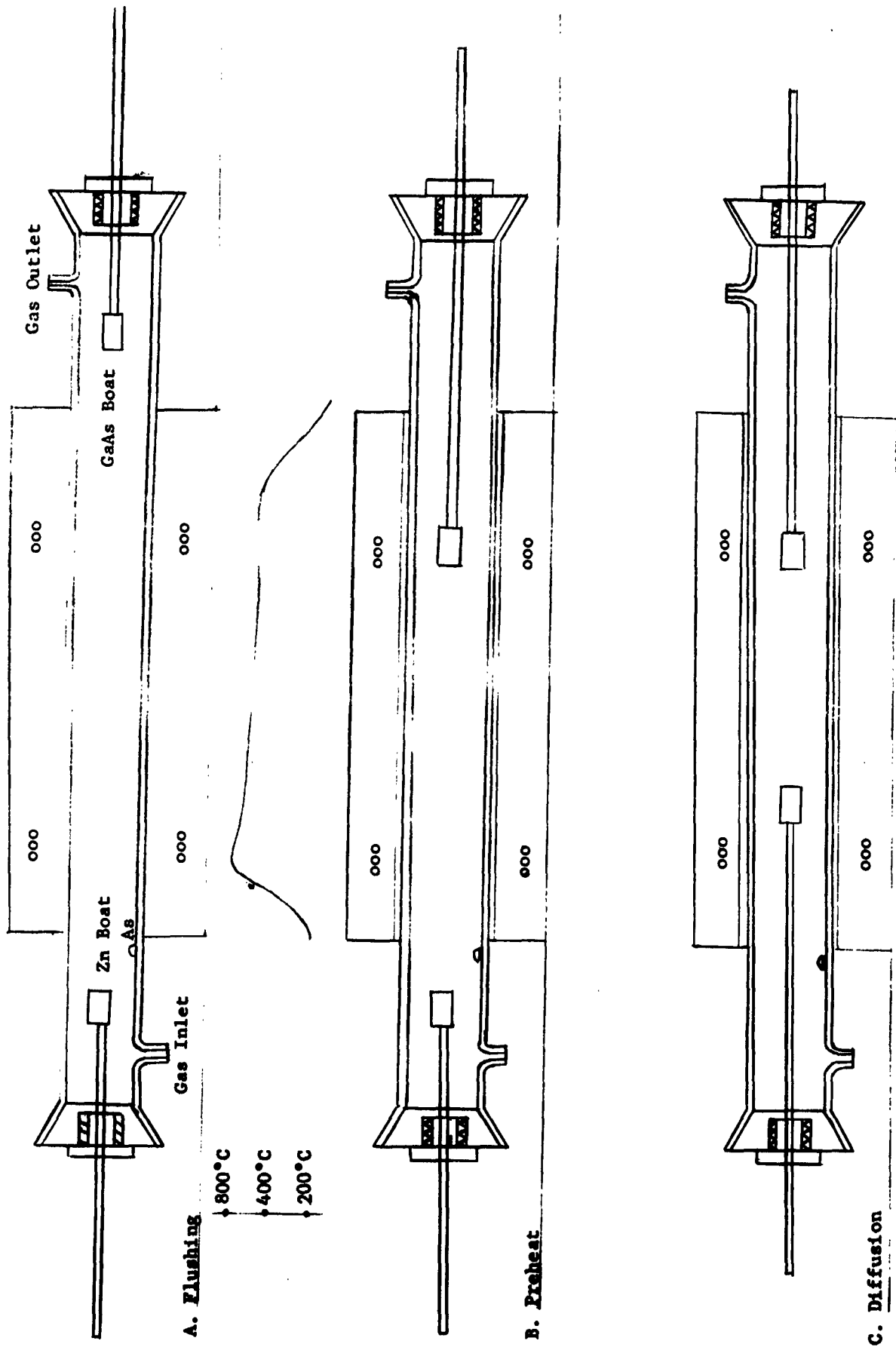
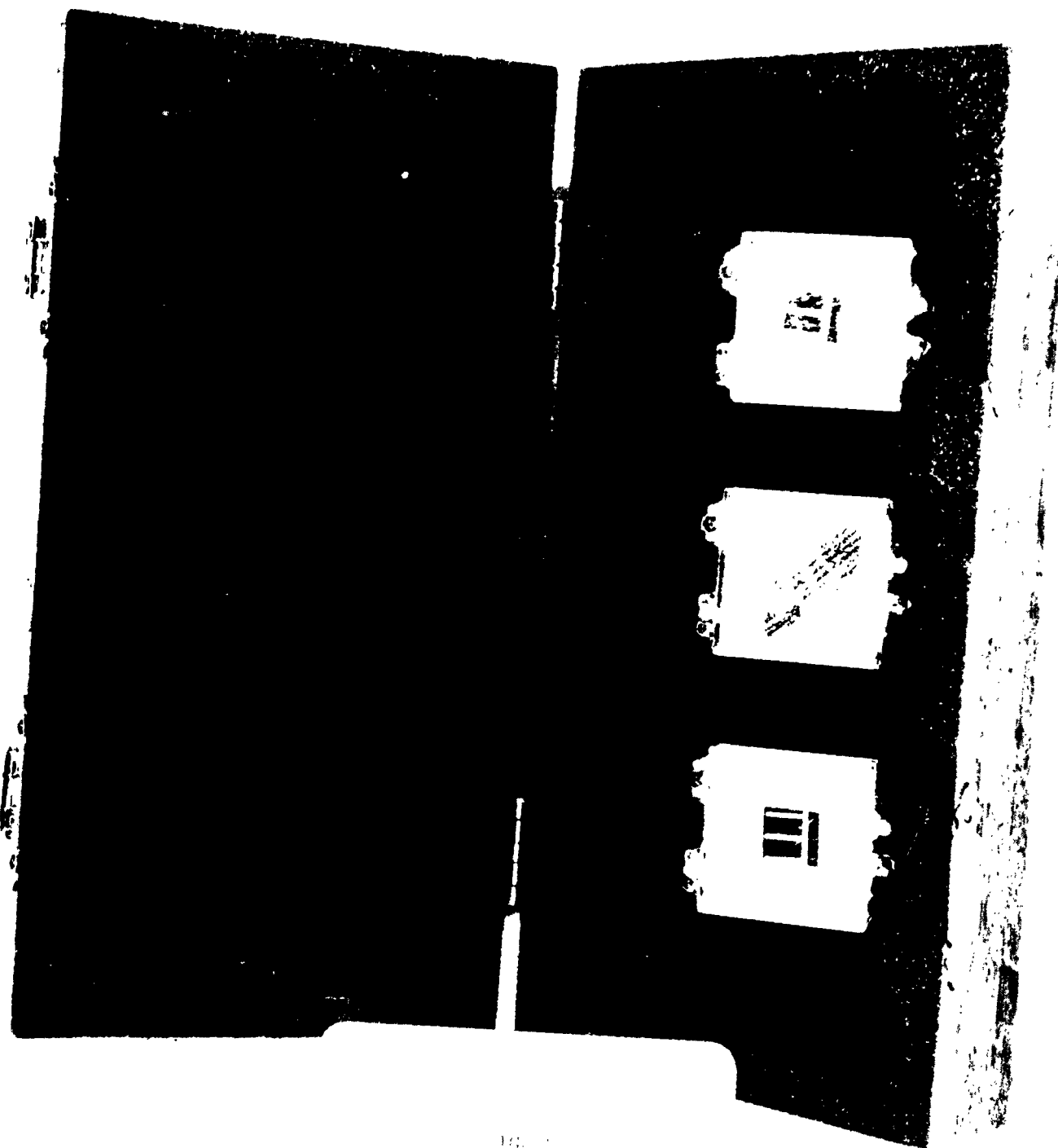


FIGURE 4



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Youngwood, Pa.

--SOLAR CELLS

BULK MATERIAL

1. Lifetime _____
2. Resistivity _____ ohm-cm
3. Dislocation Densities _____
4. Sheet Resistance _____
5. Comments _____

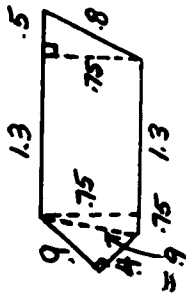


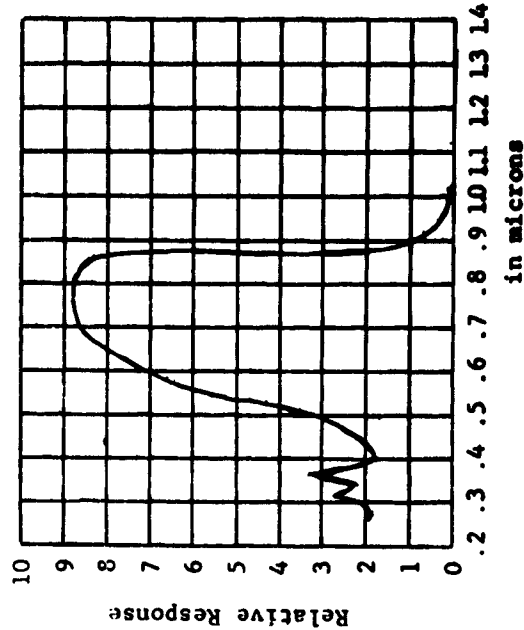
TABLE I

Sample Number Special
Date February 25, 1963
Sample Dims. L 1.3 cm W 0.8 cm
T 0.075 cm
Thickness of Diffused Layer 0.075 cm
Area 1.39 cm²
Coverage _____

FABRICATED CELL Light Intensity 0.8 suns DXC 500 Voltage ~120 Color Temp. ~3400°K
Lamp Used DXC 500 Tungsten Type Filter Used 3cm deionized water

1. R_{series} 1.85 ohms
2. R_{shunt} 1800 ohms
3. V_{OC} 0.66 v
4. I_{SC} 10.0 ma
5. V_m 0.36 v
6. I_m 7.2 ma
7. P_m 2.592 mw
8. R_{1m} 50 ohms
9. C.F. .393
10. η 2.3 %
11. J 7.2 ma/cm²
12. J_{before} _____ μ sec.
13. J_{after} _____ μ sec.

Note all units in cgs system. See reverse side for special test results.



Date Taken _____ by _____

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